Abandoning Mineral Acid

Attractive wastewater treatment alternatives quickly taking shape for industry

By Stefanie Gregg

Many industrial operations with highly alkaline wastewater that discharges into public waterways are moving away from mineral acid treatment systems. While hydrochloric (HCl) and sulfuric acid (H_2SO_4) have effectively neutralized alkaline waste streams for decades, environmental, regulatory and cost factors are making carbon dioxide (CO_2) gas diffusion treatment an attractive alternative.

Reducing alkalinity is a faster and smoother reaction with CO_2 than with mineral acid. As tiny CO_2 gas bubbles diffuse and react with the water, carbonic acid is formed to create a mild buffering agent and lower pH. The carbonic acid rapidly dissociates into hydrogen ions and bicarbonate. It is a dynamic process with CO_2 gas absorption and carbonic acid neutralization and buffering reactions occurring at the same time. Yet it also is controlled: The buffer acts as a natural brake as the reaction reaches equilibrium around the neutral point (pH 7 to 5).

Acid Indigestion

Alkaline wastewaters are generated in meat, food and beverage processing operations; pulp and paper mills; and many other chemical and industrial operations. Highly basic chlorine or sodium hypochlorite solutions often are used in bleaching operations. Equipment for processing fats, plant matter and other biological or organic compounds, in particular, often are cleaned with high pH solutions. Wastewater discharges exceeding National Pollutant Discharge Elimination System-permitted pH levels must be reported, and plants are subject to environmental fines—and public scrutiny.

Of course, some industrial plants produce mineral acids as a byproduct, and neutralizing alkaline wastewater with acids can be a logical approach to solving two discharge problems at once. For the many industrial processors that purchase mineral acids on the merchant market, however, the past few years have seen prices spike for both HCl and H_2SO_4. Transportation is a significant part of the cost of mineral acids (on the order of 50% for HCl), and costs for diesel and other fuels are trending upward. This exerts greater pressure on distributor pricing.

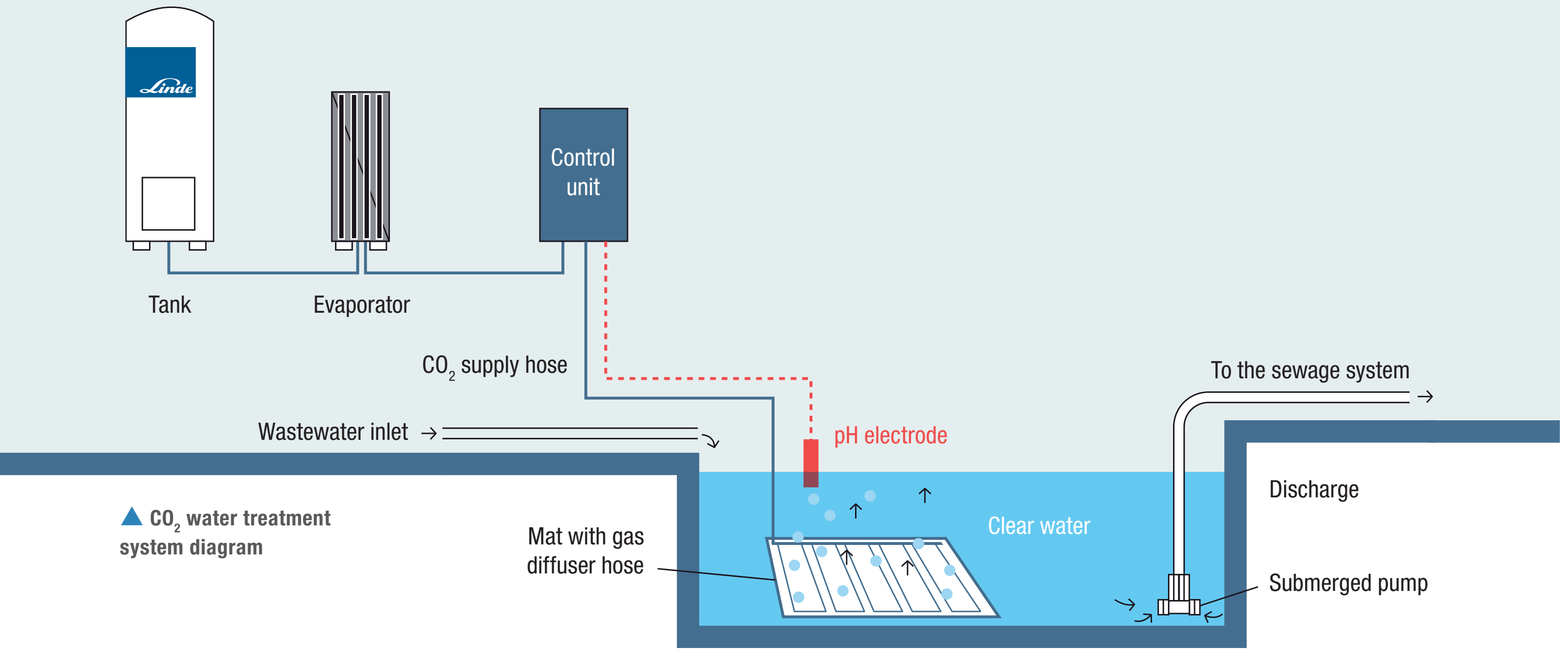
Beyond raw material costs are storage, safety and handling issues. The highly corrosive acids can take a toll on storage and processing equipment. Worker safety and maintenance procedures are constant concerns. Unexpected pipe or equipment failures can cause injuries and quickly drive up operating costs and worker compensation claims.

Linde gas diffusion water treatment pond

A Question of Control

Mineral acid treatment systems require careful titration to avoid overshooting pH discharge targets. Still, unexpected variations in plant processing or treatment parameters can inadvertently push effluents into the red zone. Acid treatment systems are particularly sensitive to changes around the neutralization point. Once that line is crossed, even small additions of acid can cause a runaway drop in pH that can overwhelm a treatment system, disrupt plant operations and require days of high-volume alkaline addition and mixing to restore balance. Meanwhile, production is lost, discharge fines accrue and corporate reputations are at stake.

Further, consumers in increasing numbers are considering environmental issues in purchasing decisions, and most major corporations already have established sustainability programs. Minimizing or eliminating the use of hazardous chemicals in wastewater treatment



▲ CO_2 water treatment system diagram

systems not only supports sustainability goals, it can dramatically reduce risks. Small- and mid-size industrial processors also are recognizing the soft and hard costs involved with these risks and uncertainties, and moving toward sustainable alternatives.

Carbon dioxide gas diffusion systems can be easy to implement. It should be noted that CO_2 treatment also is important for reverse osmosis and remineralization systems, so CO_2 site supply can do double duty.

A CO_2 treatment system for alkalinity control includes gas supply, related piping, gas metering, injection and a control system. Carbon can be injected in any one of several different ways, depending on the size and configuration of the facility. Carefully metered amounts of gas can be injected into process wastewater through diffusion mats at the bottom of treatment ponds, or directly into wastewater pipes through high-volume spray nozzles. An engineered system lowers pH in a highly controlled way and offers advantages over mineral acids, including:

Reduced treatment times. Treatment times can be slashed 80 to 90% or more, or completely eliminated with in-line systems for low to moderate wastewater flow rates.

Elimination of hazardous materials. CO_2 gas is nontoxic and noncorrosive. It requires no special protective gear or handling equipment, no special leak monitoring during deliveries and no special emergency spill-response plans.

Improved process control. Precise feedback and control systems provide highly accurate pH control and minimize CO_2 consumption. And, due to the natural buffering action of CO_2 treatment, pH cannot be pushed below 5 even with excessive dosing.

No sulfates or chloride byproducts. Carbon dioxide neutralization does not produce acid-reaction byproducts that can foul or corrode equipment internals and create other downstream control concerns. (CO_2 gas treatment is not recommended for calcium-containing wastewaters due to calcium carbonate precipitates, though mineral acid treatments may produce sulfate sludges.)

Lower overall treatment costs. Due to increasing raw material and environmental costs for mineral acids, CO_2 wastewater treatment systems are highly competitive. In many cases, capital and operating costs may in fact be lower for an equivalent system, especially when "soft costs" are considered.

When engineering a system, a number of process variables are considered. These include wastewater constituents, activity coefficients, starting pH range, buffering capacity, flow rates and pH treatment target range. A precision feedback system is essential for maximizing system efficiency while minimizing CO_2 consumption. The feedback loop monitors upstream wastewater flow rates and other variables to signal the metering system for the controlled injection of CO_2 gas as pH control proceeds to equilibrium.

Supply advantages often can be a deciding factor. Bulk supply options include pipeline or onsite storage with deliveries from regional distribution facilities by railcar or tanker truck. Carbon dioxide also can be supplied on site by rail or tanker for short-term emergency use.

To fully optimize a system, gas-supply arrangements can be set up to streamline supply logistics and level treatment costs. Linde, for example, is a commercial producer of CO_2 in North America. Carbon dioxide is extracted from natural wells or captured and recycled as a byproduct of other processes such as ethanol production. With a gas-supply arrangement, additional advantages may accrue to industrial plants such as pharmaceuticals and food and beverage processors that already use CO_2 gases for process treatment. **iWWD**

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Gas injection system